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To cite this article: A D Nikitin *et al* 2019 *J. Phys.: Conf. Ser.* **1369** 012029

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5th International Workshop on Heat/Mass Transfer Advances
for Energy Conservation and Pollution Control
August 13-16, 2019, Novosibirsk, Russia

Effect of steam supply to the air-blown gasifier on hot syngas desulphurization

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Abstract. The IGCC technology serves to efficiently produce thermal and electrical energy with minimal impact on the environment. In operating IGCC, wet desulphurization is used at temperatures below 200°C. The use of hot desulphurization at temperatures around 500°C will significantly improve IGCC efficiency. The preferred sorbent for hot gas cleaning is ZnO. At temperature of 450-500°C, ZnO begins decomposing because of reactions with syngas components (primarily hydrogen). Steam impedes reaction of ZnO with H₂ and increases ZnO thermal stability. Syngas H₂/H₂O ratio is determined by gasifier operation mode. The purpose of this work is to determine maximum temperature of hot gas cleaning depending on condition of ZnO-sorbent thermal stability and steam-air-blown mechanically activated coal gasifier operation mode. To determine the effect of steam supply to syngas composition, experiments were performed on entrained-flow gasifier (1 MW). Experimental results were processed using thermodynamic analysis to determine idealized syngas composition and CFD-modeling to determine real experiment process parameters. Syngas H₂O content was determined by CFD-modeling results. Study of ZnO-sorbent thermal stability depending on H₂ concentration and syngas H₂/H₂O ratio was performed by TGA. As a result of experimentally confirmed thermodynamic calculations, ZnO-sorbent thermal stability was found to increase to 815°C due to steam dilution.

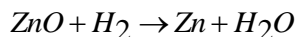
1. Introduction

The IGCC technology allows producing thermal and electrical energy with high efficiency and with minimal impact on the environment [1, 2]. The main IGCC unit is a solid fuel gasifier; and its operation mode affects the performance of all subsequent units, including gas cleaning, shift reactor (if pre-combustion scheme is used) and gas turbine unit (GTU). The composition of syngas depends on the type of gasifier: oxygen, steam-oxygen, air, etc. The steam-oxygen-blown and steam-air-blown syngases have increased humidity due to incomplete conversion of steam [3, 4]. An increase in syngas humidity improves a number of IGCC indicators: a growing rate of water shift reaction in the shift reactor increases its efficiency, and an expanding working fluid of the gas turbine improves its performance [5].

In operating IGCC, wet desulphurization is used at temperatures below 200°C. The use of hot desulphurization at temperatures around 500°C will significantly improve the efficiency of the IGCC cycle [6]. However, the problem of choosing a sorbent for hot gas cleaning has not been solved yet [7,



8]. The most preferred sorbent for hot desulphurization at 350-500°C is ZnO [9]. The upper limit of application is determined by the thermal stability of ZnO in the syngas. In the temperature range 450-550°C, a noticeable decomposition of ZnO begins as a result of interaction with H₂ [9]:



In addition to H₂, CO, CO₂ and N₂, the syngas supplied to desulphurization always contains H₂O due to incomplete fuel gasification and excess steam supply to the gasifier. In accordance with Le Chatelier's principle, steam should prevent the ZnO decomposition reaction, increasing its thermal stability, respectively.

Studies of thermal stability of ZnO-sorbents were carried out either in pure gases [10, 11] or in model mixtures [12, 13], close to the design regime for a particular gasifier. At that, the composition of the syngas changes significantly depending on the operating mode and design of the gasifier. The aim of the work is to determine the thermal stability of the ZnO-sorbent to hydrogen destruction depending on the operation mode of the steam-air gasifier operating on mechanically activated fuel. Mechanoactivation of fuel is a promising method of improving the efficiency of the gasification process [14].

2. Materials and methods

2.1. Materials

In experiments on steam-air-blown gasification, the bituminous Kuznetsk coal of D grade was used. Technical and elemental composition of coal is given in table 1.

Table 1. Technical and elemental composition of bituminous Kuznetsk coal.

W, %	A, %	V, %	C ^{daf} , %	H ^{daf} , %	O ^{daf} , %	N ^{daf} , %	LHV, MJ/kg
19.0	17.6	43.5	75.6	5.7	16.4	1.8	19.3

*daf – dry and ash free

Thermal stability was determined for the ground ZnO-sorbent, Katalco Johnson Matthew 32-4, fraction of 0-200 µm. Neither pre-drying nor calcination was realized. The composition of the ZnO-sorbent according to scanning electron microscopy is shown in table 2.

Table 2. Composition of ZnO-sorbent, Katalco Johnson Matthey 32-4.

ZnO, % wt.	Fe ₂ O ₃ , % wt.	Al ₂ O ₃ , % wt.	CaO, % wt.
94.42	0.63	3.55	1.41

2.2. Steam-air-blown gasification of mechanoactivated coal

For the study of steam-air gasification of mechanoactivated coal, a steam-air-blown entrained-flow gasifier of the Institute of Thermophysics of SB RAS with a capacity of 1 MW (for fuel) was used [14]. The first stage of the gasifier is a swirler, which is fed with mechanoactivated coal and blast air at room temperature (25°C). The second stage is the cylindrical reaction chamber, in which the steam superheated to 200°C is axially supplied through the nozzle. Mechanical activation of coal occurs immediately before the fuel supply to the gasifier in the disintegrator mill by grinding to a fraction of 0-70 microns. The average particle size is 18-30 µm. Due to mechanical activation, the ignition time is reduced and the combustion rate of coal increases, which eliminates additional heating of the air blast and the walls of the gasifier. The temperature regime is controlled by four thermocouples installed along the axis of the reaction chamber. The syngas composition is determined by a multicomponent gas analyzer TEST-1.

To determine the effect of steam supply on the syngas composition, two series of gasifier launch were realized. Before the gasification mode, the gasifier was heated in the mode of complete fuel combustion to a wall temperature of 1200°C. In the gasification modes, the fuel flow rate was 20 kg/h, the air flow rate was 40 m³/h (the stoichiometric factor was 0.42), and the steam flow rate was 0, 0.235 and 0.5 kg of steam per kg of fuel.

2.3. Determining the thermal stability of ZnO-sorbent

To study the effect of the syngas composition on the thermal stability of the ZnO sorbent, a series of non-isothermal experiments was carried out on the complex for thermogravimetric analysis (TGA), including the NETZSCH STA 449F3 device, the QMS 403C Aëolos quadrupole mass spectrometer and auxiliary equipment. The mass spectrometer was used to determine the composition and flow rate of gases at the outlet of the device. For this purpose, the mass spectrometer was in advance calibrated for mixtures of each measured gas (H₂, CO, CO₂, CH₄, N₂, O₂, H₂O) and argon. As a result, the correction factors were obtained for normalizing all ion currents of the mass spectrometer by argon. During the experiment, argon was fed with a constant flow rate to protect the block of scales; the flow rate and composition of the air blast were determined by the flow rate of argon and the ratio of normalized ion currents. Argon to protect the scales was supplied from below in counter flow to the main blast coming from the top. As the results of CFD modeling show, the shielding gas does not reach the sample and does not affect the conversion rate.

The weight of the sorbent sample was 25 mg. The heating was carried out to a temperature of 1000°C at the rate of 15°C/min. The flow rate of the mixture gas was 100 ml/min flow, and the flow rate of argon to protect the scales was 20 ml/min. Series of experiments were carried out with hydrogen dilution with inert gas (argon) and steam. The boundary of thermal stability (the temperature of the beginning of intense decomposition of ZnO) was determined by the dimensionless reaction rate:

$$R_{\tau} = \frac{1}{m_{\tau} - m_{end}} \cdot \frac{dm}{d\tau} > 0.0001,$$

where m_{τ} is the mass of the sample at the current time, and m_{end} is the mass of the inert residue.

2.4. Thermodynamic modelling

Thermodynamic modeling of thermal stability of ZnO and equilibrium composition of reaction products was performed using the entropy maximization method [15].

2.5. CFD-modelling

The paper uses the CFD model of entrained-flow gasification of solid fuel proposed in [16, 17]. The modeling was carried out on an unstructured grid with 550 thousand of computational elements. The (standard) $k-\epsilon$ turbulence submodel, the verification of which is given in [18], is used. Discrete radiation submodel (32 rays) with the submodel of "gray" gases was applied. The heterogeneous response model is the diffusion-kinetic one with kinetic constants, obtained by the device for thermogravimetric analysis (TGA) using the method of [18]. The number of calculated trajectories of fuel particles is 2000. On the walls of the setup, the no-slip condition is fulfilled.

3. Results and discussion

3.1. The influence of steam supply on conversion of mechanically activated coal

The composition of the syngas obtained by steam-air-blown gasification as a result of variation of the steam-fuel ratio is presented in table 3. Figure 1 shows the calculated dependence of the amount of steam coming out of the gasifier on the amount of steam supplied to the gasifier. From figure 1 it may be seen that the steam output from the gasifier in all modes is 95-99% of the steam at the inlet due to

low initial temperature of the steam and short time of its residence in the gasifier. A serious contribution to the steam content in the syngas is due to the high fuel humidity and in the absence of steam supply; the humidity of the syngas is 10%.

Table 3. The effect of steam on the composition of products of mechanoactivated fuel conversion (data from CFD simulation are verified against the experimental data).

Steam flow rate, kg/kg of coal	H ₂ O, % vol.	CO ₂ , % vol.	CO, % vol.	H ₂ , % vol.	N ₂ , % vol.	Q _i ^{raw} , MJ/m ³	Q _i ^{dry} , MJ/m ³
0	10	13.5	5.6	1.9	69.0	0.91	1.01
0.235	20	11.2	7.0	2.5	59.3	1.15	1.44
0.5	26	9.2	7.1	3.1	54.7	1.23	1.66

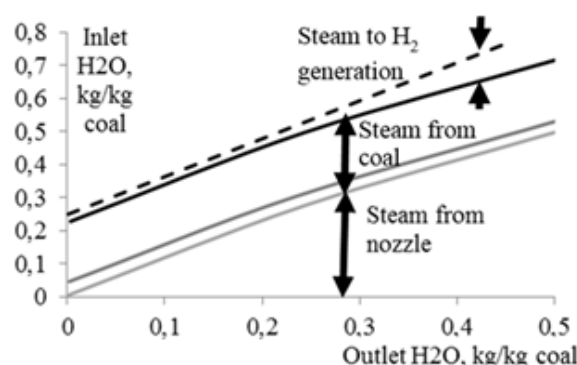


Figure 1. Dependence of the amount of steam from the gasifier on the amount of steam supplied to the gasifier.

3.2. Effect of hydrogen concentration and H₂/H₂O ratio on thermal stability of ZnO sorbent

The figure 2 demonstrates the curve of the sorbent mass loss during the experiment in pure hydrogen and the composition of gases at the outlet of the TGA device. There one may see a large excess of air blast. The figure 3 *a* shows curves of the sorbent mass loss when diluting pure hydrogen with an inert gas (argon), and the figure 3 *b* – when diluting with steam. With an increase in the proportion of argon, the rate of the sorbent decomposition and the temperature of the beginning of intense decomposition decrease due to reducing concentration of hydrogen reacting with ZnO. With an increase in the proportion of water, the temperature of the beginning of intense decomposition increases in comparison with dry hydrogen. Figure 4 demonstrates the comparison of the effect of argon and steam on the interaction of the sorbent with hydrogen according to TGA data and thermodynamic calculations. Thermodynamic estimates of thermal stability coincide with experimental data. The figure 5 shows the dependence of thermal stability of the sorbent in hydrogen on the R_t value when it is diluted with argon and steam. It may be seen that the presence of a small amount of water significantly increases the thermal stability of the sorbent.

3.3. Determining thermal stability of ZnO-sorbent for investigated modes of steam-air-blown gasification of mechanoactivated coal

Table 4 shows the maximum permissible temperature of hot gas cleaning using ZnO-sorbent for the obtained modes of steam-air-blown gasifier according to two criteria: the concentration of H₂ and the ratio H₂/H₂O in the syngas. For the obtained modes, the presence of excess steam in the syngas allows increasing the thermal stability of the ZnO sorbent from 500 to 810-815°C.

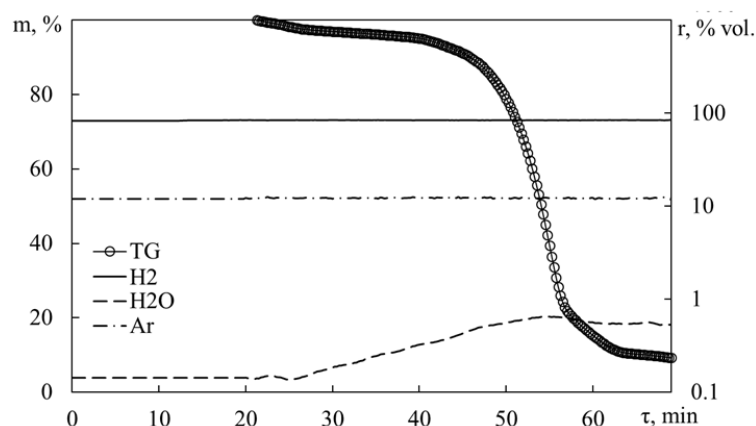


Figure 2. The loss of sorbent in pure hydrogen and the composition of gases at the outlet of the TGA.

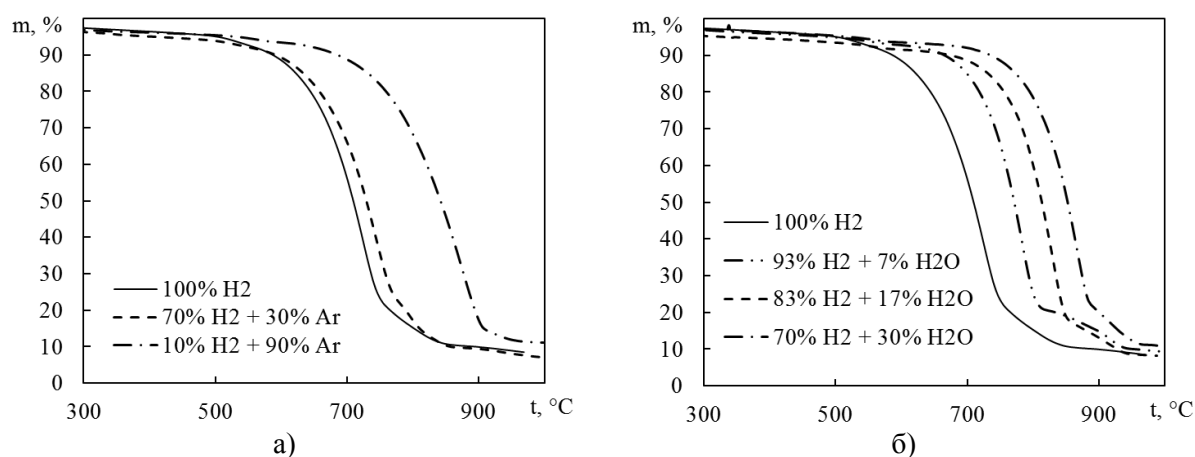


Figure 3. The curves of the sorbent mass loss at hydrogen dilution with argon (a) and steam (b).

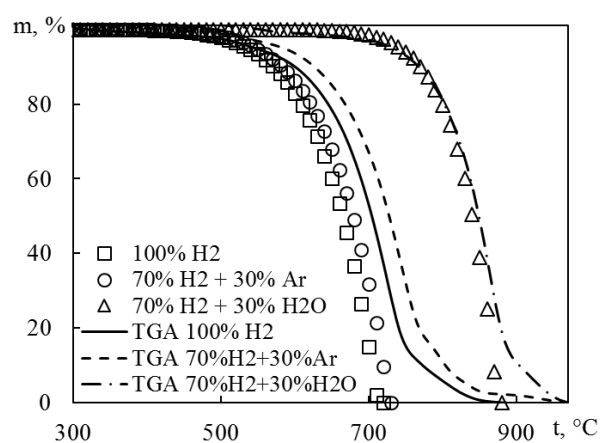


Figure 4. The effect of argon and steam on the interaction of sorbent and hydrogen: lines – experiment, dots – calculation.

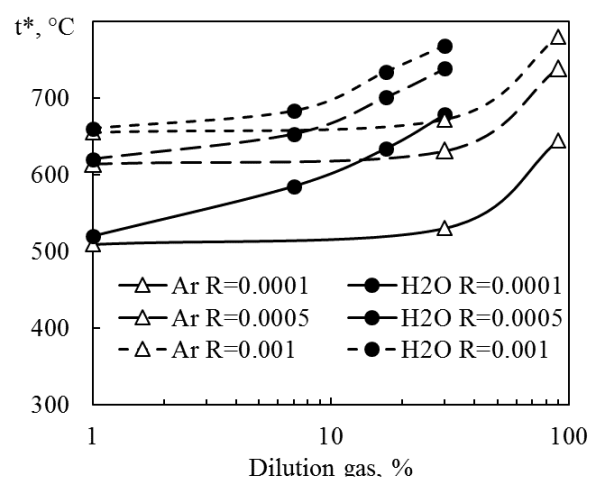


Figure 5. The dependence of thermal stability of the sorbent in hydrogen on the value of $R\tau$ at dilution with argon and steam.

Table 4. The effect of steam supply at steam-air-blown conversion of mechanoactivated fuel on the temperature of gas cleaning using ZnO-sorbent.

No. of the operating mode of the gasifier	Steam-fuel ratio, kg/kg	H ₂ /H ₂ O ratio in syn-gas	Temperature limit depending on concentration of H ₂ , °C	Temperature limit on the ratio H ₂ /H ₂ O, °C
1	0	0.19	720	790
2	0.235	0.13	715	810
3	0.5	0.12	710	815

4. Conclusion

As a result of experimental calculation (CFD) and studies of steam-air-blown conversion of mechanoactivated coal in a gasifier of a semi-industrial scale, the dependence of the conversion mode on the steam-fuel ratio has been obtained. With increasing steam flow rate, the concentration of combustible components and steam in the syngas increases. At that, a significant part of the supplied steam does not participate in chemical reactions and passes through the gasifier.

The dependence of thermal stability of the ZnO-sorbent on hydrogen concentration in the syngas and the ratio H₂/H₂O, obtained experimentally (TGA) and confirmed by thermodynamic calculations, has shown that the increase in the H₂/H₂O ratio in the syngas allows increasing the thermal stability of the ZnO-sorbent to hydrogen destruction. At that, a low steam content in the syngas (10% vol.) increases the thermal stability by 100°C. For the investigated modes of operation of the steam-air-blown gasifier using mechanoactivated coal, the temperature of syngas desulfurization by ZnO-sorbent under the condition of thermal stability of the sorbent is 790-815°C.

Acknowledgements

The work was supported by Act 211 Government of the Russian Federation, contract № 02.A03.21.0006.

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